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APPLICATION OF THE PRINCIPLE OF SIMILARITY TO CHEMICAL PROCESSES

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APPLICATION OF THE PRINCIPLE OF SIMILARITY TO CHEMICAL PROCESSES

- USSR -

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I. Similarity Criteria for Chemical Processes

The design of reactors for use with chemical processes requires usually a combined examination of the following system of differential equations set up for an infinitesimally small reactor element: 1) material balance equation; 2) energy balance equation; 3) fundamental equation of hydrodynamics or equation of motion; 4) kinetic equation of the reaction; and 5) equations associated with the determination of homologous conditions.

Even in the absence of chemical reactions it is not usually possible to arrive at an analytic solution to a system of these equations, hence in such cases the principle of similarity finds broad application.

The application of the principle of similarity to chemical processes requires joint examination of a system of all the differential equations enumerated above, supplemented by terms which take into account the presence of point sources of energy and mass, which considerably complicates the problem. The complexity resides in the fact that in the usual case it is not possible to satisfy simultaneously the hydrodynamic, thermal, diffusion, and the purely chemical similarities of the processes existing in apparatus of various scales.

It is characteristic of chemical processes that one system cannot be modeled upon another, as this can be done for physical processes.

Thus, in the case of hydrodynamic similarity, if we can preserve the constancy of the Re criterion in the model and in the prototype by replacing one system by another, this we are not able to achieve in the instance of chemical similarity, since a chemical reaction of a given group of compounds cannot in the general case be reproduced with the compounds of another group.

As a consequence of this and other difficulties, the principle of similarity at the present time is relatively rarely employed for modeling chemical processes. However, it has found quite wide usefulness in enriching experimental data of quite diversified processes (1).

As a result of similar transformations of the system of differential equations, the following criteria for chemical similarity have been obtained (2-5):

Damköhler Criterion I

$$Da_I = \frac{Ul}{cw}. \qquad (1)$$

where U = reaction rate in kg mole/(m^3)(hour); l = linear dimension in the flow direction in m; w = linear velocity of the flow in m/hour; and c = reactant concentration in kg mole/m^3.

Since l/w characterizes the residence time of the flow in the reactor, then the ration c/U will represent the duration of the reaction proceeding at constant velocity.

Consequently, the Da_I criterion can be regarded as the ratio of the residence time in the reactor to the duration time of the reaction at constant velocity until the reactant is completely consumed. It is natural that the Da_I criterion may be treated also as the ratio of the

reaction rate to the flow velocity, expressed in the same units [See Note] or as the ratio of the concentrations of the reacting substance to the concentration brought into the flow, or, of course, as the ratio of the actual length of the reactor to the length of the reactor that is necessary for the full completion of the reaction at constant velocity.

Damköhler Criterion II

$$Da_{II} = \frac{Ul^2}{cD}, \qquad (2)$$

where D = coefficient of molecular diffusion in m^2/hour.

[Note: The criterion $W = w_x/U_k$, discovered by Matz[6], involves the reaction rate U_k expressed in units of the flow velocity or, for a first-order reaction, in the form of the rate constant; as follows from the determination of the Da_I criterion, the Matz criterion is identical to the same.]

The Da_{II} criterion represents the ratio between the rate of the chemical reaction and the velocity of molecular diffusion. By analogy with the Da_I criterion the Da_{II} criterion can be treated also by use of other quantities, as this has been shown above.

Damköhler Criterion III

$$Da_{III} = \frac{qUl}{c_p \gamma w \Delta t}, \qquad (3)$$

where q = thermal effect of the reaction in kcal/kg mole; c_p = heat capacity at constant pressure in kkcal/(kg)(°C); γ = specific weight of the medium in kg/m^3; Δt = characteristic temperature difference, which can be considered as, for example, the difference in temperature between the reactor wall and the center of the flow, or the change in temperature along the length of the reactor.

As follows from ratio (3), the Damköhler criterion III is expressed as the ratio between the amount of heat released as a result of the reaction and the amount of heat transported by the flow.

Damköhler Criterion IV

$$Da_{IV} = \frac{qUl^2}{\lambda \Delta t}, \qquad (4)$$

where λ = thermal conductivity of the reaction mixture in kkcal/(m)(hour)(°C).

The Damköhler criterion IV can be expressed as the ratio between the amount of heat released as a result of the reaction and the amount of heat transported due to thermal conductivity.

Criterion of Equilibriumness or Criterion of Quasistaticity(Ž)

$$Pa = \frac{U_{B_2}}{U_{B_1}} = \frac{k_{обр} c_{B_1}^{\beta_1} c_{B_2}^{\beta_2}}{k_{пр} c_{A_1}^{\alpha_1} c_{A_2}^{\alpha_2}} \qquad (5)$$

where k_1 and k_2 = corresponding forward and reverse reaction rate constants; U_{B_1} and U_{B_2} = corresponding forward and reverse reaction rates; c_{B_1} and c_{B_2} = concentrations of the reaction products B_1, B_2, ...; C_{A_1} and C_{A_2} = concentrations of the starting components A_1 and A_2; β_1 and β_2 = stoichiometric coefficients of the reaction products; α_1 and α_2 = stoichiometric coefficients of the components A_1 and A_2.

The criterion of equilibriumness can be expressed as the ratio between the internal rates of the chemical reaction, that is, between the rates of the forward and the reverse reaction.

Criterion of Contact

$$Ko = \frac{U_{B_1}}{U_p} = k_{пр}^{\Sigma\alpha - 1} \cdot \tau \qquad (6)$$

where τ = residence time of the reaction mixture in the reactor; $\Sigma\alpha$ = the total of the stoichiometric coefficients on the right-hand side of the kinetic equation.

The criterion of contact is expressed as the ratio between one of the internal rates of the reaction and the net reaction rate.

For an irreversible reaction, when the reverse reaction is practically equal to zero, the contact criterion coincides with the Da_I criterion, which we can arrive at by employing in the Da_I criterion, instead of the reaction rate U, its expression in terms of the reactant concentrations.

It has also been suggested that the dimensionless equilibrium constant be employed as a criterion.

Arrhenius Criterion(3,6)

$$Ar = \frac{E}{RT}, \tag{7}$$

where E = energy of activation; and R = gas constant.

The Ar criterion is expressed as a ratio between the energy of activation and the internal energy of the system.

Criterion of Radiation (7)

$$K_{p_1} = \frac{qcw}{C_0 e T^4}; \tag{8}$$

$$K_{p_2} = \frac{T_1}{T_2}, \tag{9}$$

where C_0 = constant in the Stefan-Boltzmann radiation equation; e = emission coefficient in the same equation; T_1 and T_2 = corresponding temperatures of the more and the less heated surfaces.

Criteria (8) and (9) are obtained not from the fundamental system of differential equations but from the Stefan-Boltzmann equation and must be employed when the reaction occurs at a sufficiently high temperature that it is necessary to calculate for the heat transferred by radiation.

Criterion of radiation (9) can be expressed as a ratio between the quantity of heat released due to the reaction and the quantity of heat transported due to radiation, and secondly, as the ratio between the temperatures of the radiating surfaces.

Criterion of Hydrodynamic Acceleration(8):

$$K_T = \frac{w}{\Delta V}, \qquad (10)$$

where ΔV = increase in volume occurring in the course of the reaction in m^3/kg mole.

The criterion of hydrodynamic acceleration K can be expressed as a ratio between the volume of the reaction mixture which passes through the reactor in a unit of time and a change in the volume due to the chemical reaction. The criterion takes into account the acceleration of motion of the reaction mixture in the reactor which results from the progress of the chemical reaction. Both the radiation criterion and the criterion of hydrodynamic acceleration are involved in the number of criteria specified in the situation of the occurring reaction.

Still other criteria may be employed which take into consideration the specifics of the environmental conditions of the ongoing reaction.

Generalized Heat Criterion

$$K_T = \frac{qcw}{q_{cT}}, \qquad (11)$$

where q_{cT} = heat flow through a unit of heat-exchanging surface in kcal/(m^2)(hour).

This criterion is expressed as the ratio of the quantity of heat released due to the reaction and the quantity of heat exiting or entering through the heat-exchanging surface.

The expediency of introducing the K_T is conditioned by the fact that the heat flow per unit of heat-exchanging surface is independent of the variable which the experimenter may vary independently from the scale.

It is not rare in the analysis of chemical processes to employ criteria analogous to those examined earlier, though somewhat modified appropriately to the processes under study.

Thus, the following criterion (9,10) has also been introduced

$$K_{RRT} = \int_0^{\tau} c^{n-1} k_n [T(\tau)]\, d\tau \qquad (12)$$

where k_n = nth order reaction rate constant, represented as a complex function of time (it is assumed that the temperature changes according to a determined manner). It is obvious that the criterion K_{NRT} can be regarded as a modified Da_I, in which the chemical reaction rate, changing in time, is taken in the integral form. The representation of the criteria in the integral form is expedient in all cases where the properties of the chemical system are changing in time (or in space; then the integration is carried out throughout the volume).

For the case of heterogenous chemical reaction the following criterion can be introduced (11):

$$K_{rx} = \frac{k_n' \delta}{D} c^{n-1} = \frac{k_n' l}{D} c^{n-1} f(\mathrm{Re}, \mathrm{Pr}) \qquad (13)$$

where k_n' = rate constant of the heterogeneous chemical reaction occuring per unit surface of the phase boundary, and Pr = (wl)/a·Re is the Prandtl criterion, where $a = \lambda / c_p \gamma$, = coefficient of thermal diffusivity.

In the capacity of the linear dimension in this criterion we can employ the thickness δ of the diffusion film, which is equal to

$$\delta = l/\mathrm{Nu} = l f(\mathrm{Re}, \mathrm{Pr}).$$

It is not difficult to see that the criterion K_{rx} is a modification of the Da_{II} criterion in which for l δ is employed and the reaction rate is considered per unit of surface at the phase boundary.

For the same type of modified criteria it is possible to bring in the dimensionless multiplier φ, which is used in the calculation of absorption processes (12):

$$\varphi = \frac{x}{\mathrm{tgh}\, x}, \qquad (14)$$

where

$$x = \delta \sqrt{k_1/D} \qquad (15)$$

The expression (14) is obtained as a result of the combined solution of the diffusion equation and the kinetics equation for a first order reaction. The criterion (14) can be conveniently labeled as the Hatta criterion (Ha).

However, it is not difficult to show that the Hatta criterion has the same value functionally associated with the Da_{II} criterion:

$$Ha = \frac{x}{\operatorname{tgh} x} = \frac{\delta\sqrt{k_1/D}}{\operatorname{tgh}\delta\sqrt{k_1/D}} = \frac{\sqrt{k_1\delta^2/D}}{\operatorname{tgh}\sqrt{k_1\delta^2/D}} = \frac{\sqrt{Da_{II}}}{\operatorname{tgh}\sqrt{Da_{II}}} \qquad (16)$$

Simplex criteria are often used as controlling criteria. We can indicate the following in the capacity of such simplexes (3,6,12)

$$X_1 = \frac{c_H}{c_K} \qquad (17)$$

$$X_2 = \frac{c}{c^*}. \qquad (18)$$

where c_H = concentration at the reactor inlet; c_K = concentration at the reactor outlet; c = actual concentration achieved in the given reactor; and c^* = equilibrium concentration.

Simplex (17) characterizes the ratio of the concentrations at the inlet and outlet of the reactor, whereas simplex (18) characterizes the relative product yield.

Instead of the ratio of the concentrations, we can utilize the ratio of any other physical properties (10) which are characteristic of the system and which are related to the concentrations. (For example, the ratio of viscosities, densities, etc.) Such a method of replacing concentrations by physical properties can be utilized for finding out the conditions controlling the process, its regulation, and its automation.

Along with the above-enumerated similarity criteria arising from the original system of differential equations, we can include in the general criterion equations criteria which characterize the hydrodynamic similarity $Re = (wl)/\nu$, the thermal similarity criterion $Pe = (wl)/a$, and the diffusion similarity criterion $Pe_Д$

$$Pe_Д = \frac{wl}{D}, \text{ etc.}$$

Then the general criterion equation for a chemical process acquires the form for the case of irreversible reactions:

$$Da_I = f(Da_{II}, Da_{III}, Da_{IV}, Pe, Pe_A, Re, K_i \ldots) \quad (19)$$

where K_i = criteria specified by the situation of the ongoing process (cf equations (8) - (10)).

We may also employ as a determining criterion, instead of the Da_I criterion, the simplex-criteria (17) and (18).

The criterion equations in the case of reversible reactions are represented in the following form:

$$Pa = f(Ko, Da_{II}, Da_{III}, Da_{IV}, Pe, Pe_A, Re, K_i) \quad (20)$$

(The criterion Ar does not increase the number of criteria entering into the general criterion equation since it characterizes the change in the temperature value which has already been included in the criteria examined earlier: Da_I—Da_{IV}).

Since in some criteria expressed in equations (19) and (20) some of the same parameters are found, then, accordingly, the number of criteria can be diminished by combination of individual criteria.

For example, the criterion Da_{II} can be expressed as the product $Da_I \cdot Pe_A$, that is:

$$Da_{II} = \frac{Ul^2}{cD} = Da_I \cdot Pe_A = \frac{Ul}{cw} \cdot \frac{wl}{D} = \frac{Ul^2}{cD};$$

the Da_{III} criterion -- as the product $Da_I \cdot \frac{qc}{c_p \gamma \Delta t}$, that is:

$$Da_{III} = \frac{qUl}{c_p \gamma w \Delta t} = Da_I \cdot \frac{qc}{c_p \gamma \Delta t} = \frac{Ul}{cw} \cdot \frac{qc}{c_p \gamma \Delta t} = \frac{qUl}{c_p \gamma w \Delta t}.$$

The complex of the values of $\frac{qc}{c_p \gamma \Delta t}$ has been determined by D'yakonov(3) as the criterion establishing the proportionality of the temperature and the concentration domains.

We designate this criterion in the following way: [See Note]

$$K_{TK} = \frac{qc}{c_p \gamma \Delta t} \qquad (21)$$

[Note: In several studies the criterion K_{TK} has been called the Boltzmann (Bo) criterion(14).]

The Da_{IV} criterion may be represented as the product $Da_I \cdot Pr \cdot K_{TK}$, that is:

$$Da_{IV} = \frac{qUl}{\lambda \Delta t} = Da_I Pe K_{TK} = \frac{Ul}{cw} \cdot \frac{wl}{a} \cdot \frac{qc}{c_p \gamma \Delta t} = \frac{qUl}{\lambda \Delta t}$$

Inasmuch as the criteria Pe and $Pe_Д$ can be represented in the form of the products Re·Pr and $Re \cdot Pr_Д$, then by dividing out the criteria Da_{II}, Da_{III}, and Da_{IV} in the Da_I criterion, K_{TK} and Re can be put into the form of the transformed equations (19) and (20):

$$Da_1 = f(K_{TK}, Pr, Pr_Д, Re, K_l) \qquad (22)$$

or

$$X_1 = \frac{c_n}{cx} = f(Da_1, K_{TK}, Pr, Pr_Д, Re, K_l) \qquad (23)$$

and

$$Pa = f(Ko, K_{TK}, Pr, Pr_Д, Re, K_l) \qquad (24)$$

$$X_2 = \frac{c}{c'} = f(Ko, K_{TK}, Pr, Pr_Д, Re, K_l) \qquad (25)$$

or

In the case of heterogeneous chemical processes several criteria (for example, the criteria Re, Pr, and $Pr_Д$) can be repeated as many times as there are phases participating in the process.

However, the presence of a large number of criteria and consequently their physical values also, which enter into the criteria in equations (21) — (24) complicates the possibility of satisfying the constancy of all the

controlling criteria.

TABLE 1

Results Based on the Basic Criteria of Chemical Similarity [See Note]

Equation of the conservation of mass

Rate of change with time	Rate of change due to convection	Rate of change due to diffusion	Rate of change due to chemical reaction	
$-\partial c/\partial \tau$	$-(w \text{ grad})\, c$	$+D\,(\text{Div grad})\, c$	$+U$	$=0$
c/τ	wc/l	Dc/l^2	U	
		$\mathrm{Da}_{\mathrm{I}} = \frac{Ul}{cw}$		
		$\mathrm{Da}_{\mathrm{II}} = \frac{Ul^2}{cD}$		

Equation of the conservation of energy

Rate of change with time	Rate of change due to convection	Rate of change due to thermal conductivity	Rate of change due to chemical reaction	
$-\partial t/\partial \tau$	$-(w \text{ grad})\, t$	$+a\,(\text{Div grad})\, t$	$+qU/c_p\gamma$	$=0$
t/τ	wt/l	at/l^2	$qU/c_p\gamma$	
		$\mathrm{Da}_{\mathrm{III}} = \frac{qUl}{c_p\gamma w \Delta t}$		
		$\mathrm{Da}_{\mathrm{IV}} = \frac{qUl^2}{\lambda \Delta t}$		

TABLE 1 (continued)

Equation of the reaction kinetics

Resulting reaction rate	Rate of the forward reaction	Rate of the reverse reaction	
$-dc/d\tau$	$+k_{np}c^{\alpha_1}_{\lambda_1}c^{\alpha_2}_{\lambda_2}\cdots$	$k_{ob}c^{\beta_1}_{\mu_1}c^{\beta_2}_{\mu_2}\cdots$	$=0$
c/τ	$k_n c^{\Sigma\alpha}$	$k_{ob}c^{\Sigma\beta}$	

$$Ko = k_n c^{\Sigma\alpha-1}\cdot\tau$$

$$Pa = \frac{k_{ob}c^{\Sigma\beta}}{k_n c^{\Sigma\alpha}}$$

/Note: The single arrow indicates the denominator; the double arrow -- the numerator./

For example, it is impossible to sustain at the same time the constancy of both Re and Da_I in the model and in the prototype, since the linear velocity which figures in both these criteria is differently dependent on the linear dimension, which also enters into both these criteria, viz: under the conditions of preserving the constancy of the Da_I criterion it follows that the criterion varies inversely to the linear dimension. Hence, the direct modeling of chemical processes by producing a general criterion equation is shown to be practically impossible /See Note/. This has led to the necessity for approximation modeling. The derivation of fundamental chemical criteria is represented as set forth in Table 1 (cf page 685 /original pagination/).

/Note: The artificial decrease in catalyst activity in modeling of heterogeneous chemical processes (15)

has no practical value.7

II. Approximation Modeling

The principles of approximation modeling are derived from the fact that in the criterion equation it is necessary to include only those criteria which are related to the slowest stage of the process. The thermodynamic treatment of this problem has been accomplished by D'yakonov (3), who states that in the criterion equations it is necessary to include only such criteria as relate to non-equilibrium or quasi-static stages of the process.

As a result of separating out the limiting stage in the general criterion equation the incompatible criteria (for example, Da_I and Re) disappear, which makes it possible in principle to search for the functional relationship between the criteria.

The main possibility for isolating the limiting stage is predicated on the fact that in many cases the complicated process consists of several consecutively occurring stages. The slowest of such stages is also the limiting one.

In the field of chemical reaction kinetics, where the reactions are complicated by processes of heat- and mass-exchange it is convenient to distinguish (16) reactions that occur in the kinetic region, when the limiting stage is the same as the chemical change; reactions occurring in the diffusion region when the limiting stage is the diffusion of the reactants to the reaction zone; and, of course, reactions occuring in the diffusion-kinetic region, when the rates of diffusion and chemical change are commensurate. This is a most difficult example for modeling. The processes of heat-exchange within the system occur simultaneously with processes of chemical change and therefore cannot be determined.

We will indicate methods of determining the limiting stages (17,18).

1. Determination of the temperature coefficient for the total process rate. If by a 10° change in temperature the total process rate varies by 2-3 times (as follows from the Arrhenius law), then the limiting stage in that of chemical change. If changing the temperature by 10° results in a change in the total process rate of 1.3 times, then the limiting stage is one of mass-exchange. For intermediate instances the reaction occurs in the diffusion-kinetic region.

2. Determination of the apparent order of the reaction. If this is different from unity, then the limiting stage of the process is that of chemical change.

However, if the order of the reaction is equal to unity, the question of the limiting stage remains an open one, since the process of mass-exchange depends on the concentration also in the first degree.

3. Determination of the dependence of the total process rate on the hydrodynamic conditions of its progress.

If the process rate does not depend on the hydrodynamic conditions of its progress, then the limiting stage is that of chemical change, but if it is dependent, then the limiting stage is either the mass-exchange process, or simultaneously the mass-exchange process and the process of chemical change (that is, the reaction occurs in the diffusion-kinetic region).

1. Modeling of processes occurring in the kinetic region

In the case of a process occurring in the kinetic region the criterion equation involves only chemical criteria in which equations (22) - (25) are expressed in the following form:

For irreversible chemical reactions

$$Da_1 = \frac{Ul}{c\omega} = \text{const} \tag{26}$$

or

$$X_1 = \frac{c_\kappa}{c_\kappa} = f(Da_1) \tag{27}$$

The ratio of concentrations, as has been already noted above, can be replaced by a ratio of the physical properties of the system.

For reversible chemical reactions equations (24) and (25) are expressed in the form:

$$Pa = f(Ko) \tag{28}$$

$$X_2 = f(Ko) \tag{29}$$

For the generalization of experimental data on chemical reactions with unknown mechanisms, occurring in the kinetic region, two methods have been suggested (3).

One of these consists of drawing a graph on the basis of experimental data, using the coordinates Pa and τ (where τ = contact time of the reaction mixture). Here the experimental data related to the various temperatures and pressures lies on completely determinable curves.

The search for the functional relationship of Pa = f(Ko) is equivalent to a combination of all the the curves into one curve. Considering that $Ko = kc^{z+1}, \tau$, $k = f_1(T)$, and assuming that the reaction occurs in the gaseous phase, that is, $c = f_2(p)$, it is possible to find out the energy of activation and the order of the reverse reaction by varying the distance between these curves. With these values we can find the criterion Ko and derive graphically the dependence Pa = f(Ko), that is, to combine all curves into one.

Another method of generalization consists of searching for a functional relationship between the reaction rate and the thermodynamic potential used in this method in the capacity of the driving force, that is, in the experimentally established dependency having the form $u = kf(Z/RT)$, where k* = coefficient in dimensions of the reaction rate. In many cases this coefficient can be taken as constant. Z/RT is the analog of the Arrhenius criterion; Z = thermodynamic potential.

From equations (26) - (29) it follows that in the case of a process occurring in the purely kinetic region the process does not depend on the geometric form and dimensions of the sytem, under the conditions that the residence time in the reactor remains relatively constant, that is, the equality 1/w = constant is preserved. (This conclusion, however, loses its force if a chain reaction occurs, if the excitation or the rupture of the chain in the reaction takes place on the reactor walls, and also if the chemical change is accompanied by the release of a considerable amount of heat.)

The effect of the heat-exchange on a reaction occurring in the kinetic region can be calculated by introducing the criterion K_{TK} and the criterion K_T, which results in a criterion equation for the kinetic region, taking the form:

$$f(Da_i, K_{TK}, K_T) = 0 \qquad (30)$$

As noted above, the heat-exchange cannot be isolated in the limiting stage. Because of this, in going from one scale to another for the case of a very vigorously exothermic reaction (in avoiding complications due to the

formation of a temperature profile in the reactor) there is usually employed in the capacity of a model one of the elements of the larger reactor, if the reactor consists of several elements (for example, in the case of a reactor consisting of a system of tubes packed with catalyst, one of these tubes can be taken as such an element).

In spite of the fact that in modeling chemical processes occurring in the kinetic region it is not necessary to set aside geometrical similarity, still in a number of cases these processes still tend, for technological reasons, to preserve this kind of similarity (for example, in modeling mixers (12)).

In carrying out reactions releasing or absorbing a large amount of heat, which reactions occur in geometrically similar apparatus, the complication arises involving the fact that with an increase in the reactor dimensions, while preserving geometrical similarity, the ratio of the heat-exchange surface to its volume is decreased, which indicates that the conditions for the intake and the outgo of heat are deteriorated. For accomplishing approximation modeling in such cases it has been recommended (7) to artificially the value of the heat flow per unit of heat-exchanging surface in the model reactor by means of adiabatizing the reactor. This can be achieved through building the insulation layer at the heat-exchanging surface in the laboratory reactor or by introduction of supplementary heating. Such a method makes it possible, in spite of the difference in values of the heat-exchanging surface in the model compared to that in the prototype, to attain this objective: that, per unit of time the same amount of heat is supplied to both reactors per unit of volume.

It is necessary to consider also yet another difficulty which arises in modeling continuous-operation reactors. This difficulty lies in the fact that different portions of the reaction mixture in many vessels which are operating continuously reside in the reactor for different lengths of time, that is, in such a reactor a definite distribution of residence times will be established. This affects the course of the reaction with an especially strong negative effect when the basic chemical reaction is complicated with similar reactions occurring successively. Thus, in modeling continuous chemical processes for production in the model and in the prototype, both having similar yields, it is necessary to satisfy the equality of the residence time distributions.

In the study of heterogeneous chemical reactions (the determination of reaction mechanism, the determination of optimal temperature conditions for conducting the reaction, etc.) it is important to develop in the labora-

tory apparatus such conditions which would preclude or reduce to the minimum diffusion resistance, that is, the reaction would proceed in the kinetic region. In achieving this it is very important to evaluate as fully as possible the diffusion resistance and, consequently, as precisely as possible the experimental data in the determination of the reaction rate.

The application of the principle of similarity makes it possible to utilize the following methods (20). The dependence of the resulting reaction rate U_r on the weight velocity of the flow G under condition that the residence time in the reaction zone is constant can be determined. /See Note/.

/Note: Satisfying the preceding condition is tantamount to recognizing that simultaneously with an increase in the weight velocity the height of the catalyst layer is increased by the same number of times./

As follows from the preceding the kinetic region must correspond to that portion of the $U_r = f(G)$ curve, where U_r becomes constant and does not depend, or depends very slightly, on further increase in G. In the latter case we can evaluate a portion of the diffusion resistance in the following manner. Equating U_r to the quantity of substance transferred through the diffusion layer, we obtain:

$$U_r = k_r F_m \Delta p_A \tag{31}$$

where U_r = reaction rate, expressed in terms of the number of rearranging moles of component A occurring per unit time and per unit catalyst mass; k_r = coefficient of mass transfer in the gaseous phase; F_m = surface per unit catalyst mass; and Δp_A = difference between partial pressures of component A in the diffusion layer.

On the other hand, the coefficient of mass transfer k_r figures in the generalized equation of Chilton and Colburn(21), modified appropriately to heterogeneous reactions by Hougen(20):

$$j_d = \left(\frac{k_r \cdot M_m p}{G}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3} = a_0\left(\frac{\sqrt{F_p}G}{\mu}\right)^{-n} \tag{32}$$

Solving simultaneously equation (31) and (32) for $\Delta p_A/p_A$ we obtain:

$$\frac{\Delta p_A}{p_A} = \frac{1}{a_0}\left(\frac{\sqrt{F_p}\,U_r M_m p}{p_A \mu F_m}\right)\left(\frac{\mu}{\rho D_{Am}}\right)^{2/3}\left(\frac{\sqrt{F_p}\,G}{\mu}\right)^{n-1} \qquad (33)$$

In the equations set forth above: p = total pressure; p_A = partial pressure of component A; M_m = average molecular weight of the flowing gas; μ and ρ = dynamic viscosity and density of the flowing gas, respectively; D_{Am} = average coefficient of the diffusion component A in the gaseous phase; a_0 = proportionality coefficient; $\frac{\sqrt{F_p}\,G}{\mu}$ = modified criterion Re; and F_p = surface of a single catalyst particle.

The first of the criteria on the right-hand side of equation (33) is a modified Da_I criterion.

In actuality:

$$p_A/p = c'\sqrt{F_p} = 1,$$

(where c' = concentration in moles) $\mu F_m \backsim v^*$ (v is expressed in m/sec) has a certain conditional velocity, since μ is in (kg)(sec)/m^2 and $F_m = m^2/(\text{kg mass}) = \frac{m^2 m}{\text{kg force sec}^2}$.

In such a fashion equation (33) can take the form:

$$\frac{\Delta c'}{c'} = \frac{1}{a_0} Da_I Pr_A^{2/3} Re^{n-1} \qquad (34)$$

where the values of a and n depend on the Re criterion.

The values of a and n are shown as follows:

when $Re < 620$, $a_0 = 2.44$, $n = 0.51$

when $Re > 620$, $a_0 = 1.25$, $n = 0.41$

On the basis of equation (33), and that derived from it -- equation (34) -- a graph is plotted in coordinates of $\frac{\Delta p_A}{p_A} = \frac{1}{a_0} Da_I Pr^{2/3}$. The Re number is brought in as a parameter. By doing this, for each value of Re we obtain lines drawn from the origin at different angles.

Choosing the limits of precision to which the actual chemical reaction rate must be determined and the difference

$\Delta p_A/p_A$ corresponding to it in the diffusion layer, we find the corresponding velocity of the flows at a given value of the complex $(\frac{1}{a}Da_I Pr^{2/3})$. Thus, for example, if in the given study it is permissible that the value of the reaction rate, taking into consideration the diffusion resistance, lies within the limits of precision up to 10 %, we take $\Delta p_A/p_A = 0.1$, and if the precision must lie within limits up to 1 %, then the corresponding $\Delta p_A/p_A = 0.01$. In an analogous fashion we can evaluate the temperature gradients in the boundary layer.

2. Modeling processes occurring in the diffusion region

In this case the criterion equations (22) and (23) take on the form:

$$Da_I = f(Re, Pr) \tag{35}$$

Here we can employ also the simplexes X_1 and X_2 as determining criterion.

The modeling of processes occurring in the diffusion region results therefore in the utilization of the well-known criteria of physical similarity and will not be investigated here.

3. Modeling processes occurring in the diffusion-kinetic region

Included in these processes, in the first place, are heterogenous chemical processes, -- processes of catalysis and of absorption accompanying the chemical reaction.

Here, due to the incompatibility of the criteria Da_I and Re, which enter in equations (22) and (23) the principal difficulty arises when employing these equations for modeling. This difficulty makes more imperative the need to take into account the resistances in each phase, by means of introducing criteria for each phase. However, this difficulty may be avoided.

Usually the same catalyst is employed both in the model and in the prototype (with identical granulometric composition) or the same dessicant. For this reason, the volume elements formed by adjoining catalyst grains or dessicant are identical in the model and in the prototype. However, in this regard it should not be overlooked that for small values of the ratio d_a/d_0 (diameter of apparatus

d_a to the grain diameter d_0) it is necessary to consider wall effects. This permits an immediate transfer of results obtained in the model over to the prototype, if conditions of carrying out the experiments (load per cross-section of the apparatus, temperature, concentration, etc.) are kept constant and if d_a/d_0 is sufficiently large.

If the reaction is accompanied by the release of large quantities of heat, the reactor must be divided into elementary reactors of small diameter in order to increase the ratio of the external heat-exchanging surface of the reactor to its volume and thereby obviate the possibility of insufficiently high temperatures developing inside the reactor. Usually in such cases a reactor is used which consists of a system of small diameter tubes. The diameter is chosen from a calculation of the production of the permissible difference in temperatures between the heart of the flow inside the tube and its walls, corresponding to the production of maximum yield(22).

In modeling it is necessary to take into account also the previously expressed consideration concerned with the basis for employing equation (30).

At the present time in determining the resulting reaction rate, which reaction occurs in the diffusion-kinetic region, equations are used that are analogous to those employed for the calculation of the processes of simple mass-transfer uncomplicated by chemical reaction, that is, the resulting kinetic coefficient is determined as the reciprocal value of the sum of the resistances in each of the phases. Here the individual coefficients of mass-transfer for each phase can be determined from the corresponding criterion equations for these phases.

Hence, in the case of a heterogeneous chemical reaction, the resulting reaction rate can be calculated from the equation(23):

$$G_a = k_э c_г = \frac{1}{\frac{1}{k_г} + \frac{C}{d}\frac{1}{k' F_0 \rho_к \Phi}} \cdot c_г \qquad (36)$$

where: $k_э$ = effective rate constant of the heterogeneous chemical reaction; $c_г$ = concentration of the chemically active component in the gaseous phase; $k_г$ = coefficient of mass-transfer in the gaseous phase; and C/d_0 = ratio of the volume of the catalyst grain to its external surface. For spherical grains C = 6; k' = rate constant of

a reaction occurring per 1 cm^2 of the total catalyst surface; F_0 = total surface of 1 g of catalyst; ρ_K = apparent of the porous catalyst mass; ψ = coefficient of the degree of utilization of the catalyst surface, taking into account the drop in concentrations of the corresponding component inside the pores of the catalyst.

For a very rapid reaction, this occurs almost exclusively on the external surface of the catalyst grains, and in that case $\psi \longrightarrow 0$. For a very slow reaction, this involves the entire surface of the catalyst grains, including the surface of the internal pores, in which case $\psi = 1$.

Thus, in equation (36) the value of ψ is always less than 1.

The second item in the denominator takes into account along with purely chemical resistance the diffusion resistance inside the pores of the catalyst grains. Several studies(24) have calculated the diffusion resistance inside the pores separately from the chemical resistance. In such a case the denominator includes three items. Such a form of the equation is less convenient for practical use.

Similar equations are employed in calculating for absorption processes (25,26) that accompany chemical reactions, and also for processes of heterogeneous catalysis in the liquid phase(24).

For the case of a slow irreversible first-order chemical reaction occurring in the liquid phase volume, the following equation(27) has been proposed:

$$G_a = K_{or}\left(p - \frac{p_x}{\cosh x}\right) = \frac{1}{\frac{1}{k_r} + \frac{1}{\varphi H k_x}}\left(p - \frac{p_x}{\cosh x}\right) \qquad (37)$$

where H = Henry's constant; k_{or} = total mass-transfer coefficient for mass transferred into the gaseous phase; and p_x = partial pressure of absorbent in the liquid phase volume.

It is necessary to note that in absorption processes accompanying chemical reactions in the presence of processes of heterogeneous catalysis, the chemical reaction occurs as a rule not on the surface of the phase boundary, but in the zone adjoining this surface, which has a finite thickness. Therefore the process of chemical change and the process of diffusion in the liquid phase proceed not successively but simultaneously, which leads to a continuous decrease in the diffusion flow of the absorbing component to the extent of its passage through the diffusion layer

in the liquid phase. This circumstance also leads to a certain complication in the form of equation (37) in comparison with equation (36).

It has been suggested that the criterion Ha be employed, also, for the calculation of absorption processes accompanying reactions of the second and higher orders (12,28).

III. Scale Equations

A consequence of the use of principles of approximation modeling are the so-called scale equations (2,7,14, 29,30).

The scale equations are obtained by equating pairwise criteria which characterize the environment of the ongoing process, in the model and in the prototype, and an elimination in these criteria of the physical constants that remain constant in the model and in the prototype.

We set forth the derivation of the scale equation for the chemical process that occurs in the kinetic region and which is complicated by heat-exchange. As has been indicated above, the general criterion equation for such a process can be set forth in the form:

$$f(\mathrm{Da}_I, K_{TK}, K_T) = 0 \tag{30}$$

To preserve the similarity of the limiting stage in the model and in the prototype requires the preservation of the constancy of all criteria which characterize this stage. To obtain the scale equations let us equate pair-wise for the model and for the prototype all the criteria entering into equation (30):

$$(\mathrm{Da}_I)_M = (\mathrm{Da}_I)_\Pi \tag{38a}$$

$$\frac{U_M l_M}{c_M w_M} = \frac{U_\Pi l_\Pi}{c_\Pi w_\Pi}, \tag{38b}$$

where the indexes M and indicate, respectively, that the given values refer to the model and to the prototype.

Eliminating the physical constants, and considering that the concentrations (for example, initial or final) remain unchanged in the model and in the prototype, we obtain for the criterion Da_I:

$$\frac{l_M}{w_M} = \frac{l_\Pi}{w_\Pi} \tag{39}$$

From the equation obtained it follows that in the model and in the prototype the residence time must be identical.

For the criterion $K_T = \frac{qcw}{q_{CT}}$ we obtain:

$$\frac{w_м}{w_п} = \frac{(q_{CT})_м}{(q_{CT})_п} = \frac{l_м}{l_п} \qquad (40)$$

The criterion $K_{TK} = \frac{qc}{c_p \gamma \Delta t}$ includes only physical constants and therefore it yields no new ratios.

In an analogous fashion we can produce scale equations for other limiting stages. Thus, in the case of the heterogeneous chemical reaction occurring in the purely kinetic region, there enter into the criterion of the scale equation: the catalyst activity α and the volume velocity s (1/sec). For this case we have:

$$(Da_I)_м = (Da_I)_п \text{ или } \frac{k'_м f(c_м)\alpha_м}{w_м} = \frac{k'_п f(c_п)\alpha_п}{w_п} \qquad (41)$$

Where k' = rate constant of the heterogeneous chemical reaction occurring per unit catalyst surface.

Introducing the volume velocity s (1/sec), we obtain:

$$\frac{k'_м f(c_м)\alpha_м}{(d_0)_м s_м} = \frac{k'_п f(c_п)\alpha_п}{(d_0)_п \cdot s_п} \qquad (42)$$

where d_0 = diameter of the catalyst grain when $\frac{\alpha_M}{\alpha_П} = 1$ and when $(d_3)_M = (d_3)_П$ (the size of the granules are taken as constant since the change in granule dimension, as a rule, is related to catalyst activity), we obtain:

$$s_м = s_п, \qquad (43)$$

that is the volume velocity in the model and in the prototype must be equal; it has been suggested also(30) that in deriving the scale equation for the case of the chemical reaction occurring in the kinetic region, due to the need to calculate for the heat-exchange it is necessary to employ the criterion Da_{IV} in conjunction with the thermal criterion Nu. We set forth the derivation of this equation

appropriately for a homogeneous chemical reaction occurring in a tubular reactor.

Equating:

$$\frac{(Da_{IV})_M}{Nu_M} = \frac{(Da_{IV})_n}{Nu_n}$$

we obtain:

$$\frac{q_M U_M d_M^2}{\lambda_M \Delta t_M Nu_M} = \frac{q_n U_n d_n^2}{\lambda_n \Delta t_n Nu_n} \tag{44}$$

where d_M and d_Π = diameters of the tubular reactors employed, respectively, for the model and the prototype. Assuming that the quantity of product processed in the prototype is n times greater than that for the model, we obtain the following relationship:

$$n d_M^2 w_M = d_n^2 w_n \tag{45}$$

from which:

$$n = \frac{d_n^2 w_n}{d_M^2 w_M} \tag{46}$$

Considering also the need to preserve the constancy of the criteria Da_I in the model and in the prototype, we obtain:

$$\frac{U_M l_M}{c_M w_M} = \frac{U_n l_n}{c_n w_n} \tag{38b}$$

Considering, in addition, that the identical yields in the model and in the prototype can be produced under conditions of identical increases in temperature ΔT in both systems, then for a tubular reactor:

$$Nu = const\, Re^{0.8} \tag{47}$$

From equation (44) we obtain:

$$\frac{d_M^{1.2}}{w_M^{0.8}} = \frac{d_\Pi^{1.2}}{w_\Pi^{0.8}} \tag{48}$$

From equation (38b) it follows that $\frac{l_M}{w_M} = \frac{l_n}{w_n}$ (39)

Solving simultaneously equations (45), (48), and (39) we finally obtain:

$$d_п = d_м \cdot n^{0,288} \tag{49}$$

$$l_п = l_м \cdot n^{0,428} \tag{50}$$

$$w_п = w_м \cdot n^{0,428} \tag{51}$$

In conclusion we will examine the derivation of the scale equations for the case of a homogeneous chemical reaction in the gaseous phase in a continuous-operation tubular reactor.

In the derivation of scale equations here it is necessary to take into account the fact that the pressure loss in the model and in the prototype must be equal, since in the opposite case, in the reactor where the loss of pressure will be greater, there takes place an increase in the flow of the gaseous mixture in the reaction, as a consequence of which the residence time in this reactor is diminished. Neglecting the difference in pressure losses is possible only in such cases when the total pressure in the system is large compared to pressure losses. If we represent the friction coefficient of the gaseous medium in the form of the equation:

$$\Delta p = c_1 \lambda \frac{l}{d} w^2 \tag{52}$$

and considering that

$$\lambda = c_2 \mathrm{Re}^{-m} = c_3 (wd)^{-m} \tag{53}$$

$$V_{сек} = c_4 d^2 w,$$

and that

$$\tag{54}$$

where c_1, c_2, c_3, and c_4 = constants.

As a result of the simultaneous solution of equations (52) - (54) we obtain:

$$\frac{l_п}{l_м} = \left(\frac{d_п}{d_м}\right)^{\frac{1+m}{8-m}} \tag{55}$$

$$\frac{(V_{сек})_п}{(V_{сек})_м} = \left(\frac{d_п}{d_м}\right)^{\frac{7-m}{8-m}} \tag{56}$$

[subscript of V = sec]

In a turbulent motion regime we can equate m = 0.16. Introducing this value into equations (52) and (53) we obtain:

$$\frac{l_n}{l_м} = \left(\frac{d_n}{d_м}\right)^{0.41} \tag{57}$$

$$\frac{(V_{сек})_n}{(V_{сек})_м} = \left(\frac{d_n}{d_м}\right)^{2.41} \tag{58}$$

Therefore, the ratio of the dimensions of the model and the prototype taken in a direction perpendicular to the direction of the flow motion must be larger than the ratio of the dimensions taken in a direction parallel to the flow axis. Consequently, the model tubular reactor must have the ratio of its length to its diameter as a larger value than that for the prototype. For a laminar regime of motion in both reactors, on the basis of the Poiseuille equation we can analogously proceed to the following scale equation:

$$\frac{d_n}{d_м} = \left[\frac{(V_{сек})_n}{(V_{сек})_м}\right]^{1/3} \tag{59}$$

Since the ratio of the reactor lengths is equal to the ratio of the reactor diameters, in this case geometrical similarity must be preserved; since the ratio of the volume expenditure is equal to the ratio of the cubed diameters of the reactors, the volume expenditure must be proportional to the reaction volume.

An attempt has been made(14) to model reactors on geometrical and regime parameters. The diameter of the apparatus d_a and the linear velocity of the flow motion w have been employed as fundamental parameters. These parameters have been utilized in the form of the ratio of the corresponding values in the model and in the prototype. As supplementary parameters, the ratio of which in the model and in the prototype is expressed through a ratio of the fundamental parameters, there has been employed the volume flow velocity V_{sec}, the geometric simplex d_a/l, the criterion Re, the criterion Da_I, the drop in pressures Δp, and the heat flow through the heat-exchanging surface $\pi d_a l \alpha$ or jl/d_a, where α = coefficient of heat output, and j = heat-transfer factor. Here it is assumed that the height of the apparatus varies proportionally to the linear

flow velocity, that is, that the mean residence time in the apparatus is kept constant.

In Table 2 the following designations are employed: ratio of diameters of the reactors $\frac{d_П}{d_М} = x$, ratio of reactor lengths $\frac{l_П}{l_М} = y$, ratio of the linear velocities $\frac{w_П}{w_М} = z$, and the ratio of volume velocities $\frac{(V_{secП})}{(V_{secМ})} = \beta$. These ratios have been called scale multipliers (cf Table 2).

ТАБЛИЦА 2

1 Сравниваемый параметр	2 Масштабный множитель	$x^2z=\beta$ $y/z=1$	$x=1$	$x=\sqrt[3]{\beta}$	$x=\sqrt{\beta}$	$x=\beta$
d, диаметр 3	x	x	1	x	x	x
l, длина 4	y	β/x^2	β	x	1	$1/x$
w, скорость 5	z	β/x^2	β	x	1	$1/x$
6 $V_{сек} = \pi d^2 w/4$	x^2z	$=\beta$	β	x^2	x^2	x
d/l	x/y	x^3/β	$1/\beta$	1	x	x^2
$Re = \rho wd/\mu$	xz	β/x	β	x^2	x	1
$Da_1 = k_1 l/w =$	y/z	$=1$	1	1	1	1
$= k_1 V/V_{сек}$ 6						
Δp	$yz^2/x\,(xz)^m$	$\beta^2/x^7\,Re^m$	β^{2-m}	x^+	x^{-m+1}	x^-
$\pi d l \alpha$	$y\,(xz)^{1-m}$	$\beta^2/x^3\,Re^m$	β^{2-m}	x^+	x^{-m+1}	x^-
$\mu l/d$	$y/x\,(xz)^m$	$\beta/x^3\,Re^m$	β^{1-m}	x^-	x^{-m-1}	x^-

1) comparative parameter; 2) scale multiplier; 3) diameter; 4) length; 5) velocity; 6) V_{sec}

The relationship between the scale multipliers which characterize the ratio between the fundamental parameters is expressed in the equation:

$$x^2z = \beta \tag{60}$$

Hence, by expressing the ratio of one of the fundamental parameters in the model and in the prototype through a ratio of other parameters, different scales can be obtained. Thus, when $z = \beta$, we have $x = 1$ (Table 2, column 4). This case corresponds in practice to the preservation of the constancy of the diameters of the model and the prototype.

When $z = x$, we have $\sqrt[3]{\beta}$ (Table 2, column 5). This case corresponds to geometrical similarity of the model and the prototype, owing to the equality $z/y = 1$ and $y = x$,

that is, the ratio of model and prototype lengths is equal to the ratio of their diameters.

Analogously, when $z = 1$ (Table 2, column 6) we have $x = \sqrt{\beta}$. This refers to the equality of model and prototype lengths when the ratio of the model and prototype productivities is equal to the ratio of their cross-sections.

Of course, $z = 1/x$ (Table 2, column 7), we have as a consequence $x = \beta$. This case corresponds to the case of the preservation of hydrodynamic similarity in the model and in the prototype. Actually, the condition $zx = 1$ indicates that the ratio of the criterion Re in the model and in the prototype is equal to 1 (since the physical constants are neglected, then the ratio of the criteria are shown to be equal to the product zx). In Table 2 scale relationships are displayed, which are shown to be expressed as the ratio of supplementary parameters in the model and in the prototype through a relationship of the fundamental parameters for each of four previously examined examples. This attempt is a modified method of using scale equations.

For the particular case of the heterogeneous catalytic reaction occurring in the gaseous phase over a fixed catalyst layer we can obtain the following kinetic equation(6):

$$V_{сек}\,dy = U_k(1-y)\,dF \tag{61}$$

where y = extent of change; dF = element of catalyst surface; and U_k = rate of chemical reaction expressed in units of flow velocity.

Equation (61) permits us to relate the size of the apparatus to the chemical-reaction rate and to the extent of change.

This equation is valid under the following assumptions: the chemical-reaction rate U_k is constant throughout the entire length (height) of the apparatus, the quantity of transforming substance varies along the length of the apparatus proportionally to the difference between the actual composition in a given cross-section of the apparatus and that theoretically possible, and the first-order reaction occurs without volume change.

As a result of integrating equation (61) we obtain:

$$1-y = e^{-U_k F / V_{сек}} \tag{62}$$

Equation (62) can be set forth in the form of the following relation between terms of the dimensionless

complexes:

$$A = \Gamma \cdot W \tag{63}$$

where $A = -\varepsilon/\ln(1 - y)$ is the criterion which indicates the extent of change for a given value of the utilized portion of the catalyst surface.

It is apparent that in its physical concept this criterion is equivalent to the concentration simplex X_1 or the relative yield simplex X_2.

The criterion $\Gamma = 1/l\sigma$ is the criterion of geometrical similarity for the catalyst surface. It is equivalent in its physical concept to the criterion of geometrical similarity.

The criterion $W = w/U_k$ is the criterion of kinetic similarity equivalent in its physical concept to the criterion Da_I, which has been already noted above (cf page 680) [original pagination; pp 2,3 in translation]. In the equations set forth above ε = utilized portion of the catalyst surface; σ = specific surface of the catalyst; and w = linear flow velocity.

It is necessary to note, however, that the applicability of the criterion equation (63) is limited by the limits that were set down in the derivation of the original kinetic equation. Moreover, it is assumed here, evidently, that the reaction takes place in the kinetic region, and consequently, that the process of mass-exchange does not have a retarding influence on the reaction.

The analogous equation for the case of a first-order homogeneous reaction has been set forth by Pozin(31) in deriving an equation for the determination of the efficiency of the chemical apparatus (for the latter Pozin took the degree of approximation to the theoretically possible results that was achieved in the apparatus). The Pozin equation is of the following form for this case:

$$\eta = 1 - e^{-k_1 fl / V_{сек}} \tag{64}$$

where η = efficiency of the chemical apparatus; f = cross-section of the flow (apparatus); and l = flow length.

From an examination of equations (62) and (64) it is possible to set up their analog, since the efficiency of the apparatus for the case of a first-order chemical reaction, as is clear from its determination, is identical to the degree of conversion since both equations coincide in concept. They relate the dimensions of the apparatus to the flow velocity and the degree of conversion. However,

in utilizing the equations it is important to keep in mind that both equations do not take into account neither the complication due to heat- and mass-exchange nor the distribution of residence times in the apparatus.

IV. Some Particular Examples of the Practical Use of the Principle of Similarity

Examples of the practical use of the principle of similarity for chemical processes occurring in the kinetic region has been described in a monograph by D'yakonov(3). Thus, as a result of the generalization of experimental data in the synthesis of ammonia at various temperatures the following criterion equation has been obtained:

$$X_2 = \left(\frac{bKo}{1+bKo}\right)^{1/2} \tag{65}$$

where b = constant.

In generalizing experimental data in the synthesis of ammonia at various temperatures and pressures the following equation has been obtained:

$$P_2 = \left(\frac{bKo}{1+bKo}\right)^{2} \tag{66}$$

In an analogous fashion from the generalization of experimental data for the oxidation of sulfur gas at various temperatures the following equation has been derived:

$$X_2 = \frac{Ko}{1+Ko} \tag{67}$$

With the aid of equation (67) it has been possible to combine isotherms of the so-called Knitch diagram into a single curve which describes this equation.

In the generalization of experimental data in the thermal decomposition of salts and oxides of calcium and cadmium(30) it has been shown that all processes of thermal decomposition of these oxides and salts are subsumed in the criterion equation:

$$\frac{1}{Ko} = 1 - P_2 \tag{68}$$

In generalizing experimental data for the polymerization of vegetable oils (in the production of drying oil (10)) an equation of the form following has been obtained:

$$\Phi = f(K_{\text{инт}}) \tag{69}$$

where Φ = ratio of physical constants employed for the control of the technological process (viscosities, densities, etc.).

These equations have been presented in graphic form. Their practical use makes possible a significant improvement in control of the course of the process and in the avoiding of impediments in products. In addition, it has given rise to a scheme of automation for this process, based on the equation (69) being employed herein.

As a result of the treatment of experimental data in the propagation of flame in a tube filled with burning gases mixed with various inert gases, which differ significantly one from another by reason of the diffusion coefficients and the coefficients of thermal diffusivity, the following criterion equation has been obtained(32):

$$\left(\frac{w}{\sqrt{ak_2c_2}}\right)\cdot\left[\left(\frac{qc_1}{\gamma c_pT}\right)^{2,36}\left(\frac{D}{a}\right)^{0,6}\right]=f\left(\frac{c_1}{c_2}\right) \tag{70}$$

where w = flame propagation velocity; a = coefficient of thermal diffusivity; and c_1 and c_2 = reactant concentrations (methane and oxygen). This equation has been presented in a graphical form.

It is easy to show that the criterion $\frac{w}{\sqrt{ak_2c_2}}$ is the ratio $\sqrt{\frac{Pe}{Da_I}}$. In actual fact:

$$\left(\frac{w}{\sqrt{a_2kc_2}}\right)^2=\frac{w^2l}{ak_2c_2l}=\frac{wl}{a}\cdot\frac{w}{k_2c_2l}=\frac{Pe}{Da_I} \tag{71}$$

The criterion D/a is obviously the ratio of the criteria $Pe/Pe_Д$. The criteria remaining have been already examined earlier.

Thus, a general criterion equation can be set forth also in the following form:

$$\left(\frac{Pe}{Da_I}\right)^{0,5}\left[(K_{TK})^{2,36}\cdot\left(\frac{Pe}{Pe_Д}\right)^{0,6}\right]=f(X_3) \tag{72}$$

where $X_3 = c_1/c_2$, or in the more general form:

$$f = (Da_I,\ Pe,\ Pe_д,\ K_{тк},\ X_з) = 0 \qquad (73)$$

In the generalization of experimental data for chemical reactions occurring in the diffusion region, for example, in the absorption of ammonia by sulfuric acid, processes are described by equations of the form:

$$G_a = K_{ог} F \Delta p_{ср} \qquad (74)$$

where $k_{ОГ} = k_Г$ -- the total coefficient of mass-transfer into the gaseous phase, and $\Delta p_{ср}$ = mean driving force in the apparatus, expressed in units of partial pressure.

Here, as always, the mass-transfer coefficient is found from the corresponding criterion equation for physical absorption.

In a recent study(33) generalized equations have been obtained for physical sorption processes in drying towers, taking into account the hydrodynamic condition of the two-phase system: for easily soluble gases:

$$Nu \cdot A\, Re_г^m Pr_г^n (1 + f) \qquad (75)$$

for difficulty soluble gases:

$$Nu \cdot A_1\, Re_ж^{m_1} Pr_ж^{n_1} (1 + f) \qquad (76)$$

where f = factor of the hydrodynamic condition of the two-phase system. The values of A, m, n and f depend on the hydrodynamic regime under which the two-phase system exists.

The common criterion equations of mass-transfer are utilized to determine the rates of chemical processes existing in a system of solid body-gas. For example, with the aid of the principle of similarity it has been shown (34) that the velocity of the combustion of carbon is determined by the supply velocity of oxygen through the external diffusion layer in the gaseous phase.

It is necessary to emphasize that the diffusion criterion equations can be employed also for the case of absorption accompanying a slow chemical reaction when the absorbing component proceeds without reacting, or only very slightly reacting, through both diffusion layers (in the gaseous and in the liquid phases), that is, when the reaction occurs mainly in the liquid phase volume. For such a case the reaction influences only the value of the compressibility of the vapor of the absorbing component in

the liquid phase volume, without changing the form of the equation. A number of such processes involve the absorption of ethylformate by a solution of NaOH(25).

As an example of the application of the principle of similarity to chemical processes occurring in the diffusion-kinetic region, we can offer the criterion equation:

$$Nu = C\,Ha\,Re^{3/4}Pr^{1/4}, \qquad (77)$$

which equation was obtained in a treatment of the experimental data in the absorption of carbon dioxide by an alkali solution, and solutions of soda and of diethylamine (12,28). As an example of the partial use of the similarity principle in the calculations of processes of heterogeneous catalysis, we can suggest the design of a contact tower for the production of phenol by utilization of the Raschig method(22). For computing the diffusion resistance it has been suggested here to utilize the method(20) described above by the present authors. A considerable number of examples of partial application of the similarity principle for chemical process calculations -- for processes occurring in the diffusion-kinetic region in quite diversified apparatus can be found also in other works(35-38).

As an example of the experimental confirmation of the use of scale equations we can point to the work of Bretshneyder(30), who experimentally verified the possibility of modeling reactors with the aid of scale equations. The experiments were conducted in two tubular reactors, whose dimensions were established in accordance with the requirements arising from the scale equations for a pseudo-homogeneous system which was represented by a suspension of zinc dust in a sulfuric acid-dichromate solution. The productivities of both reactors were divided into five parts each. The scale equations (49) - (51), examined in this present review, were used as the original equations, obtained under the condition of the preservation of the constancy of temperature increases in both reactors. As a result of the experiments conducted it was confirmed that in satisfying the geometrical ratios found from the scale equations, the ratios between the dimensions of the model and the prototype and the flow velocities, the actual increase in temperature in the prototype coincides with that set by the limits of error in the experiment.

In the controlling phenomenon of diffusion, that is, for processes occurring in the diffusion region, conditions have been formulated for modeling packing apparatus used for systems of gas-liquid, and vapor-liquid(39). This is made possible by the fact that the regime of the point of

phase inversion discovered in packingsleads to the simple conclusion: 1) velocities in each tower cross-section; 2) pressure drop; and 3) distribution of liquid in the tower. Thus, each layer element of the packing is replaced by a number of arranged layer elements.

In treating the same systems in the model and in the objective, the modeling of packing towers results in the satisfying of the following conditions:

For the heights of the packing layer:

$$\frac{h_1}{h_2} = \left(\frac{\sigma_2}{\sigma_1}\right)^{1.3} \left(\frac{F_{c_1}}{F_{c_2}}\right)^{1.8} \tag{78}$$

For the tower diameters:

$$\frac{D_1}{D_2} = \left(\frac{\sigma_1}{\sigma_2}\right)^{0.25} \left(\frac{F_{c_2}}{F_{c_1}}\right)^{0.75} \tag{79}$$

For the pressure drops:

$$\frac{\Delta p_1}{\Delta p_2} = \left(\frac{\sigma_1}{\sigma_2}\right)^{0.3} \left(\frac{F_{c_2}}{F_{c_1}}\right)^{0.8} \tag{80}$$

where σ = specific packing surface (packed condition) in m^2/m^3; and F_{c_i} = free cross-section or the free packing volume in m^3/m^3.

In a recent study(40) involving the use of equations (75) and (76) conditions have been found for the modeling of chemical processes.

The application of the principle of similarity to chemical processes opens up the possibility of generalizing experimental data for chemical reactions occurring in the kinetic, the diffusion, and the diffusion-kinetic regions.

In several instances, the principle of similarity has opened up the possibility of modeling chemical processes by use of scale equations and criteria presented in integral form.

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